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Morphology of irradiated PMMA membranes prepared by phase inversion with supercritical CO_2

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Abstract Poly (methyl methacrylate) (PMMA) pellets are irradiated using ^{60}Co gamma-ray in air and successfully formed by hot pressing at constant conditions. The irradiated PMMA membranes are prepared by supercritical carbon dioxide ($scCO_2$) as a physical blowing agent using the pressure quench method. Effects of foaming conditions such as adsorbed dose, saturation temperature, pressure on the morphology and cell size of the microcellular PMMA membranes are investigated in detail. The results showed that the irradiated PMMA membranes possess spherically closed-cell structure with uniform cell size. They have a high cell density compared with virgin PMMA. The cell size uniformity becomes poor at dose lower than 10 kGy, but increases with the dose at dose higher than 10 kGy. The mean cell diameter is less than 10 μm and the cell density increases with increasing dose. The average cell size of irradiated PMMA membranes decreases and cell density increases with increased saturation temperature and pressure. The changes in morphology of membranes are attributed to the gamma-ray radiation and $scCO_2$ synergistic effect.

Key words PMMA, Irradiation, Supercritical CO_2, Micropore, Morphology

1 Introduction

Poly (methyl methacrylate), PMMA, is a very useful flexible material, cheap and easy to obtain in different forms and colors. Many physical properties of PMMA such as electrical, optical, thermal and mechanical properties are modified after subjecting to a high-energy ray irradiation. These modifications in properties are due to the chemical bond scissions and/or cross-linking induced by the high-energy ray radiation. The radiolysis of PMMA has been studied more extensively than that of any other polymer. This can be probably explained by the fact that irradiation produces striking changes in PMMA that can be detected by a simple visual examination. Color changes are particularly apparent and easy to follow spectroscopically because of the perfect optical clarity of the polymer. PMMA is also used in dose measurements and aeronautical materials in intense radiation fields[1]. It is sensitive to radiation, and its chemical and physical properties are modified after gamma-ray radiation. Wall and Brown[2] reported that the number of bond scissions produced in PMMA for a given dose of gamma-irradiation was influenced by the presence of air and benzene as well as by temperature as measured by the intrinsic viscosity method. Ouano *et al.*[3] showed that the average molecular weight of PMMA decreased with increasing dose of gamma-irradiation as determined by gel permeation chromatography. Subrahmanyam[4] reported that the glass transition temperature of PMMA decreased and thermal expansion coefficient

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increased with increasing dose of irradiation. Kudoh[5] showed that the mechanical properties of PMMA were degraded by gamma-irradiation. Generally, gamma-ray radiation of PMMA causes main chain scission and hydrogen abstraction from an a-methyl or methylene group[6,7]. The extent of formation of each of the derivatives resulting from irradiation depends on the physical state of PMMA. PMMA may be taken as a model for chain scission without simultaneous cross -linking after exposure to gamma-ray radiations[8].

Microcellular polymeric material is a new class of material that typically has cell sizes in the order of 10 μm and cell densities of more than 10^9 cells/cm^3. Microcellular polymeric materials can be obtained without additional post-treatment, thus avoiding solvent-removing processes. In addition, they offer multiple advantages over solid polymers, including reduced material cost and weight, good mechanical properties and chemical resistance, low thermal and electrical conductivity, and good sound insulation[9-11]. They are found in many applications such as packing materials for column chromatography[12], spacer spheres for liquid crystal display, polymer-supported catalysts, polymer-immobilized extractants[13], templates for preparing porous inorganic microspheres [14], and carriers of enzymes[15] and drugs[16]. In recent decades, supercritical carbon dioxide ($scCO_2$) has been widely used as a foaming agent to generate microcellular polymer materials[17–24]. The products usually possess uniform pore size and high porosity, and the pore morphologies can be controlled by varying CO_2 pressure or temperature[25]. $scCO_2$ techniques have been developed to prepare microcellular PMMA foams[26,27]. Foamed PMMA products exhibit fine microcellular structures with either wholly closed or open pore cells, depending on the processing conditions and physical properties of the polymers. However, foaming irradiated PMMA using $scCO_2$ has not been reported in the literature.

In this work, PMMA samples are irradiated by gamma-ray in air at low dose, and then the membranes of irradiated PMMA are successfully prepared using $scCO_2$ as the physical blowing agent. The irradiated PMMA membranes possess spherically closed-cell structure with uniform cell size and had a higher cell density than those virgin PMMA membranes. The average cell size of irradiated PMMA membranes decreases but cell density increase with increasing saturation pressure. Membranes of irradiated PMMA at low dose may be used as packing materials, polymer-supported catalysts, polymer-immobilized extractants, and so on.

2 Experimental

2.1 Materials

PMMA pellets are purchased from CHI MEI Corporation, with a density of 1.16 g/cm^3 and melt index of 2.0 g/10 min. The pellets are dried at 50ºC in a vacuum oven for 24 h and placed in a desiccator prior to use. Carbon dioxide (>99.5%, pure) is from Loutang Special Gases of Shanghai. Anhydrous ethanol (analytical grade) is used as received.

2.2 Irradiation of PMMA

Gamma-ray irradiation is carried out in the ^{60}Co source of Shanghai Institute of Applied Physics. PMMA pellets are irradiated to 5, 10, and 20 kGy in air at room temperature, respectively. The irradiated PMMA pellets are mixed in the mixer (Thermo Haake PolyDrive, Germany) and hot pressed at 200 °C and 18 Mpa for 5 min into thin sheets 1.0 mm thick. All specimens are cut into 10.0 mm × 10.0 mm pieces for the foaming process.

2.3 Membrane preparation

PMMA sheets are placed in a beaker capped with a porous polyethylene thin film and then sealed into a high-pressure stainless steel vessel (500 mL). After the vessel is preheated to the desired temperature, CO_2 is introduced into the vessel to purge the vessel for several minutes. Then, the vessel is pressurized with CO_2 using a high-pressure liquid pump. When the desired pressure is reached, the system is kept at that pressure and temperature for 8 h. The time of exposure is sufficient for $scCO_2$ sorption into the polymer to reach thermodynamic solubility[23]. At the end of this period, the vessel is depressurized by opening valve 10 and venting the CO_2 in less than 30 s. The external temperature of the vessel is maintained constant during the depressurization step. The temperature

inside the vessel decreases as the pressure is rapidly reduced to atmospheric pressure. It is raised slowly to the set value (ca. 20 min) and kept at that temperature for about 5 min, and then, the specimens are removed from the vessel and cooled to ambient temperature.

2.4 Membrane characterization

Before characterization, all samples were placed in a desiccator for one week to let CO_2 diffuse out of the polymer matrix. Calorimetric data were determined with a DSC-7 Perkin-Elmer apparatus equipped with TAS-7 software and a Perkin-Elmer PE-7700 professional computer. The equipment was calibrated with indium (T_m = 156.6ºC and ΔH_f = 6.8 cal/g) as the standard. Samples of about 10 mg were sealed in aluminum pans and were heated from 25–200ºC at a heating rate of 10 °C/min in a nitrogen atmosphere.

Micro-structures of the microcellular PMMA materials are characterized by a LEO 1530 VP scanning electron microscope (SEM) at an acceleration voltage of 5.0 kV. The samples were immersed in liquid nitrogen and fractured at liquid nitrogen temperatures, then mounted on stubs. The fractured surfaces were sputter-coated with gold for observation.

Average cell size (D) was determined from the SEM images of the foam cross-section by using Image-Pro Plus 6.0 software (Media Cybernetics). With this method, the cell density (N_f) is determined by the number of cells per unit volume of foam, which was calculated using Eq.(1):

$$N_f = \left(\frac{nM^2}{A}\right)^{3/2} \quad (1)$$

where n, M and A are the number of cells in the micrograph, the magnification of the micrograph, and the area of the micrograph (cm^2), respectively.

The glass transition temperature (T_g) of polymers gives valuable information on the molecular structure changes. To investigate the characteristic changes of irradiated PMMA samples, typical DSC curves of virgin and irradiated PMMA specimens are depicted in Fig.1. The T_g value of virgin PMMA is 105.3ºC. The T_g of irradiated PMMA decreases with increasing dose from 5 kGy to 10 kGy. However, the T_g of irradiated PMMA specimens with 20 kGy show a slight increase.

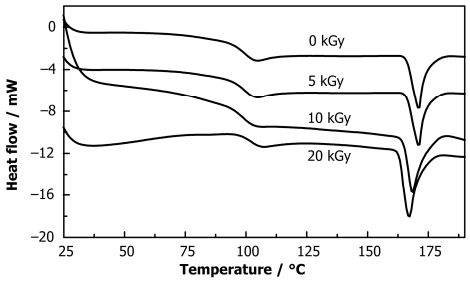

Fig.1 Calorimetrics curves of virgin and irradiated PMMA at different dose.

3 Results and discussion

3.1 Effect of irradiation on structural change

PMMA is a well known degradative polymer, whose main chains are found to suffer random degradation as a result of exposure to radiation. Previous research works on PMMA showed that the most important effect due to gamma-radiation is degradation of the polymeric chain. Subrahmanyam[4] reported that the T_g of PMMA decreases with increasing dose. It is confirmed that the main chain fracture occurs at random, at room temperature, causing a decrease in the molecular weight of the polymer with the increase of the dose and the absence of monomer products. It is proposed that for each scission of the main chain, a lateral group is disrupted with an 83% probability. Changes in the molecular structure produced by the gamma-radiation are reflected in modifications of thermal properties. But the T_g value of 20 kGy irradiated PMMA is 105.5ºC, indicating the possibility of a double bond formation in the chain ends attributed to higher energy radiolysis[8]. The chemical changes are promoted by radiation in PMMA. The melting transition temperature of irradiated PMMA decreases with increasing dose as shown in Fig.1. A decrease in the melting point implies molecular chain scission after irradiation[7]. The analysis indicates that gamma-ray irradiation causes structural change and chain scission after 20 kGy. So lower dose irradiation does not change molecular structure of PMMA, but higher dose do, and irradiation might modify the molecular structure of PMMA[8]. The molecular weight decreases with increasing dose because of decrease in the melting point of irradiated PMMA.

3.2 Effect of irradiation on morphology of membranes

Micrographs of irradiated PMMA membranes formed at various doses are investigated using SEM. The SEM images of the pristine PMMA membranes are also shown in Fig.2(a) for comparison.

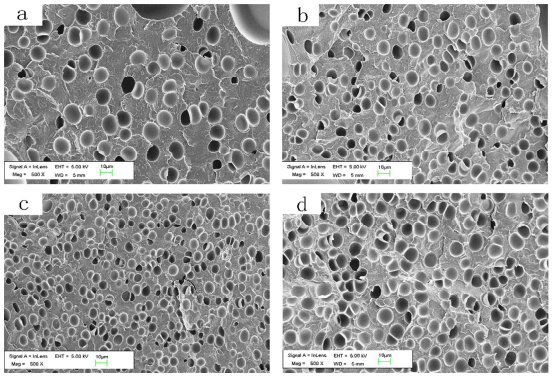

Fig.2 SEM micrographs for the irradiated PMMA foams produced at 80°C, 20 MPa and at different doses. (a) 0; (b) 5; (c) 10; (d) 20.

Figs.2(b–d) shows the SEM images of PMMA membranes foamed under different dose at constant saturation temperature (80ºC) and pressure (20 Mpa). We can see that, although the micropore were formed, they are not perfect spherical shape. As revealed in Fig. 2(a), the cells of micropore are discrete, nearly spherical and surrounded by thick walls. The depth of micropore is heterogeneous and shallow. The deep and small micropore is distributed over the virgin PMMA membranes. The formation of micropore is probably due to the desorption of some part of CO_2 during pressure quench, which leads to low CO_2 concentration near the membrane surface and restrict the growth of nuclear. The number of micropore changes with increasing dose. The depth of samples decreases with increasing dose from 5 kGy to 10 kGy. However, the depth and the cell size of irradiated PMMA membranes with 20 kGy show a slight increase and homogeneity get better from Figs. 2(b–d). Fig.3 shows the effect of dose on the cell morphology parameters of membranes. The average cell size of PMMA membranes first decreases with the increasing dose at dose lower than 10 kGy, but increases with the dose at dose higher than 10 kGy. However, cell density increased with the dose at dose lower than 10 KGy, and then decreases with the increasing dose at dose higher than 10 kGy. The cell size uniformity becomes poor at dose lower than 10 kGy, but increases with the dose at dose higher than 10 kGy. The mean cell diameter is less than 10 μm and the cell density increases with increasing dose. The change in morphology is attributed to the effect of radiation on the molecular structure of PMMA. Radiation causes structural changes in PMMA, including chain scission and hydrogen abstraction from an a-methyl or methylene group[6,7]. The chain scission leads to decrease of macromolecular chain length, resulting in lower melt strength and viscosity. During irradiation, gamma ray produces excited atoms and ions, and Coulombic interactions among these ions can cause excessive bond stretching or breakage, and nuclear reactions can cause atomic displacement. Both processes lead to the release of pendant atoms and groups such as -H, -CH_3, and CH_3OOC- and main chain scission. Thus, various gaseous molecular species are released during irradiation. The most prominent species are hydrogen, molecular scission products from the end groups as well as pendant groups of the polymer, and their reaction products. Radicals or dangling bonds are created by the release of pendant atoms such as hydrogen and by the loss of pendant groups. The micropore morphology change of irradiated PMMA is due to complicated changes of molecular structure.

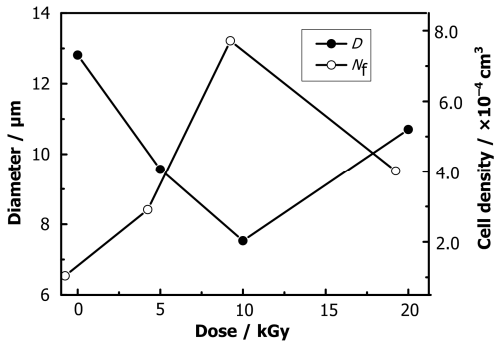

Fig.3 Effect of irradiation on the cell morphology parameters of PMMA.

3.3 Effect of saturation temperature and pressure on membranes morphology

The effect of saturation temperature is examined at constant saturation pressure (20 MPa) and the same adsorbed dose (10 kGy). Fig.4 shows the effect of

saturation temperature on the cell morphology of PMMA membranes. Fig.4(a) shows the cell size and depth is heterogeneous. The big pore cells are discrete, nearly spherica and surrounded by thick walls. The different micropore size is distributed over the PMMA membranes. The number of micropores increases with increasing temperature. The micropore size graduates homogeneous with increasing satuation temperature. The depth of micropore decreases with increasing temperature from 60ºC to 80ºC and the depth increase at temperature of 90ºC. Fig.5 shows the effect of saturation temperature on the cell morphology parameters of the irradated PMMA membranes. As saturation temperature increased, the number of smaller sized cells increases while the number of larger-sized cells decrease. The average cell size of PMMA membranes first decreases with the increasing temperature lower than 80ºC, but increases with the temperature higher than 80ºC. However, cell density increased with the temperature lower than 80ºC, and then decreases at 90ºC.

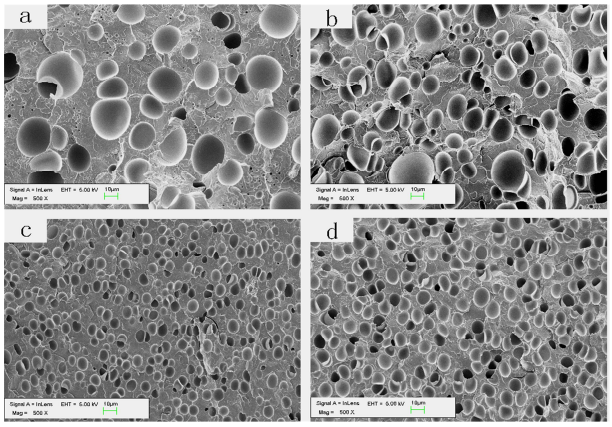

Fig.4 SEM micrographs of the irradated PMMA membranes produced at different temperature (°C): (a) 60; (b) 70; (c) 80; (d) 90.

When exposed to high scCO$_2$ pressures[23,25]. As the saturation temperature increases, the viscosity of the substrate material decreases. This will make retractive force restricting cell growth decrease and increased diffusivity of CO$_2$ within the substrate. As mentioned in the literature[26], the formation of a micropores in the foaming process, as described previously, can be attributed to gas molecules near the surface of the samples diffusing out of the sample faster than they can join nuclei. Rapid diffusion out of the sample creates a depletion layer near the surface in which the gas concentration is too low to contribute to nucleation and growth. However, in the core of the micropores, after the rapid depressurization of high-pressure CO$_2$-saturated polymer, the solubility of CO$_2$ in the polymer decreases and more CO$_2$ molecules separate from the solution. If the degree of super-saturation is sufficiently high so that the energy barrier for nucleation is overcome, new stable nuclei develop. In the absence of the super-saturation, CO$_2$ molecules diffuse into preexisting bubbles, thereby causing them to grow. These processes are competitive and depend on factors such as the quantity of CO$_2$ molecules available for nucleation, the rate at which CO$_2$ is available, the physical characteristics of the polymer-rich phase, and the interactions between the two phases[22]. Thus an open cellular structure is formed. Accordingly, the process of the formation of open cellular micropores is mainly related to the processing conditions such as saturation pressure, saturation temperature and saturation time. At a certain temperature, the nucleation and growth of micropores are slower than CO$_2$ diffusion, however the nucleation growing increase with the temperature higher than 80°C. These factors lead to cell growth and decrease cell sizes.

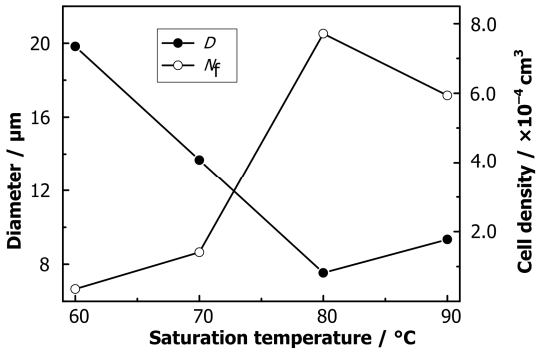

Fig.5 Effect of saturation temperature on the cell morphology parameters of the irradated PMMA membranes at different temperature.

The effect of saturation pressure on the cell morphology was studied at 80°C and 10 kGy, and the results are shown in Fig.6. Fig.6(a) shows there are some micropores in the membrane. The cell size and depth are heterogeneous. The number of micropores is graduating with increasing saturation pressure. The cell size and depth decrease with increasing pressure.

The micropores are discrete, nearly spherica and surrounded by thick walls.

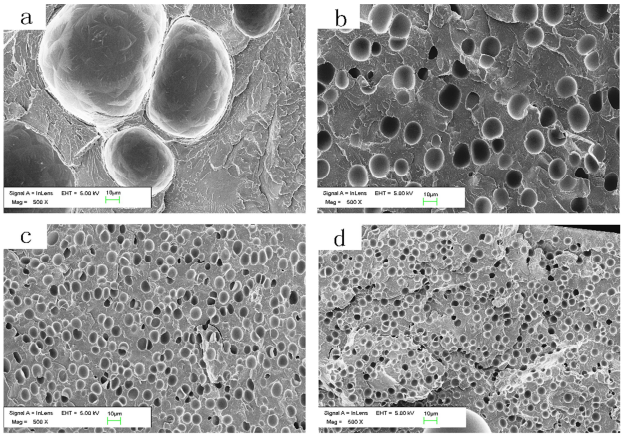

Fig.6 SEM micrographs for the irradated PMMA foams produced at different pressure(Mpa).(a)10;(b) 15; (c) 20; (d) 25.

Fig.7 shows the effect of saturature pressure on the cell morphology parameters. As the $scCO_2$ saturation pressure increases, the average cell size decreases. However, cell density increases with increasing saturation pressure.

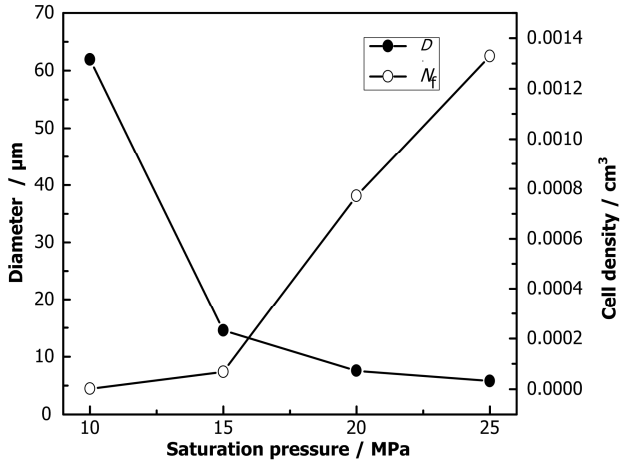

Fig.7 The effect of saturation pressure on the cell morphology parameters of the irradated PMMA foams produced at different pressure.

Microcellular PMMA membranes can be produced by foaming polymer of CO_2 using the pressure quench method. The amount of CO_2 incorporated into the PMMA also increases with increasing saturation pressure. Thus, PMMA was more highly supersaturated upon releasing pressure, which probably resulted in a large population of cells being nucleated[26]. Classical nucleation theory predicts that, as the magnitude of the pressure drop increases, the energy barrier to nucleation decreases, leading to more cells being nucleated within a given volume[26]. Consequently, irradiated PMMA micropores can be largely foamed due to CO_2 molecules diffusion. It is common to generate a closed-cell microcellular core structure encased by a nonporous skin in the $scCO_2$ foaming of bulk polymers.

4 Conclusion

The membranes morphology of gamma-ray irradiated PMMA is investigated by $scCO_2$ as a physical blowing agent using the pressure quench method for the first time. PMMA is a well known degradative polymer. The T_g of irradiated PMMA decreases with increasing dose at dose lower than 10 kGy, but increases with the dose at dose higher than 10 kGy. The melting transition temperature of irradiated PMMA decreases with increasing dose. The membranes of the irradiated PMMA possess spherically closed-cell structure with uniform cell size and have a higher cell density than virgin PMMA membranes. The cell size uniformity becomes poor at dose lower than 10 kGy, but increases with the dose at dose higher than 10 kGy. The mean cell diameter is less than 10 μm and the cell density increases with increasing dose. The average cell size of irradiated PMMA membranes decreases and cell density increases with saturation temperature and pressure. Membranes of irradiated PMMA at low dose may be widely used in industrial field.

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